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HYDROGEN EXCHANGE OF FERROCENE AND ITS DERIVATIVES [*]

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FOLLOWING a short communication[1] referring to an unpublished observation by J.O. Santer on deuteration of ferrocene in the presence of $BF_3.D_2O$, we deem it necessary to report on our investigation of hydrogen exchange of ferrocene and its derivatives in acidic media.

We found ferrocene to substitute deuterium readily for hydrogen atoms when dissolved in anhydrous deuterosulphuric acid. At the same time ferrocene was oxidized to ferrocinium cation which, however, did not take part in hydrogen exchange. Both concurrent reactions, deuteroexchange and oxidation, proceeded at different rates.

Different acidic donors of deuterium with no oxidative properties smoothly exchange hydrogen in ferrocene. Thus the isotope exchange reaction of ferrocene hydrogen runs at room temperature in such media as a

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[1] T.J. Curphey, J.O. Santer, M. Rosenblum and J.H. Richards, J.Amer.Chem.Soc. 82, 5249 (1960).

mixture of deuteroacetic and trichloroacetic acid, deuterophosphoric acid in dioxane solution, deuterated hydrochloric acid, deuterated alcohol saturated with hydrochloride, and deuterated trifluoroacetic acid.

Considering the hydrogen exchange of ferrocene and its derivatives to be one of the simplest instances of electrophilic substitution reactions, it proved of interest to estimate its kinetics in order to have a quantitative characteristic of the relative electrophilicity of the above compounds, and; in particular, to compare it with that of corresponding benzene derivatives. To this end we have studied the hydrogen exchange kinetics of ferrocene, acetyl ferrocene, and benzene in deuterated trifluoroacetic acid. At a molar ratio ferrocene (acetyl ferrocene) : CF_3COOD : benzene = 1 : 3 : 20 (at 25°, $H_o \sim -0.5$) the hydrogen exchange rate constants of ferrocene and acetyl ferrocene were found to amount to $1.62 \cdot 10^{-4} sec^{-1}$ and $1.93 \cdot 10^{-6} sec^{-1}$, respectively, * i.e. the rate of ferrocene was eighty times that of acetyl ferrocene. Under these conditions benzene was not found to be affected and the rate of toluene proved to be three orders lower than that of ferrocene.

It is believed that the investigation of hydrogen exchange of ferrocene and its derivatives in media with different degrees of acidity should result in a quantitative characteristic of the relative electrophilicity of various metallocene and aromatic systems. Such an investigation is in progress and will be reported on later.

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* The deuterium exchange rate constant of acetyl ferrocene was calculated in terms of the exchange data for all hydrogen atoms of the molecule, including the hydrogens of the methyl group.